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The issue of oxidant/ozone measurement is discussed in Part VII by James N. Pitts, Jr. of the Statewide Air Pollution Research Center, University of California at Riverside, and George Su of the State of Michigan Department of Natural Resources in Lansing. Analytical measurement techniques are compared and recommendations for improvements are made.

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INTERNATIONAL CONFERENCE ON OXIDANTS, 1976 — ANALYSIS OF EVIDENCE AND VIEWPOINTS

Part VII. The Issue of Oxidant/Ozone Measurement

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ABSTRACT

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The more than one hundred presentations and discussions at the Conference revealed the existence of several issues and prompted the EPA to sponsor a follow-up review/analysis effort. The follow-up effort was designed to review carefully and impartially, to analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere), and to attempt to resolve some of the oxidant-related scientific issues. The review/analysis was conducted by experts (who did not work for the EPA or for industry) of widely recognized competence and experience in the area of photochemical pollution occurrence and control.

The issue of oxidant/ozone measurement is discussed in Part VII by James N. Pitts, Jr. of the Statewide Air Pollution Research Center, University of California at Riverside, and George Su of the State of Michigan Department of Natural Resources in Lansing. Analytical measurement techniques are compared and recommendations for improvements are made.

CONTENTS

ABSTRACT iii

INTRODUCTION 1
B. Dimitriades and A.P. Altshuller

THE ISSUE OF OXIDANT/OZONE MEASUREMENT 3
B. Dimitriades and A.P. Altshuller

REVIEW AND ANALYSIS 7
J.N. Pitts, Jr.

REVIEW AND ANALYSIS 15
G. Su

REFERENCES 19

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INTRODUCTION

Basil Dimitriades and A. Paul Altshuller

In recognition of the important and somewhat controversial nature of the oxidant control problem, the U.S. Environmental Protection Agency (EPA) organized and conducted a 5-day International Conference in September 1976. The one hundred or so presentations and discussions at the Conference revealed the existence of several issues and prompted EPA to sponsor a followup review/analysis effort. Specifically, this followup effort is to review carefully and impartially and analyze relevant evidence and viewpoints reported at the International Conference (and elsewhere) and to attempt to resolve some of the oxidant-related scientific issues. This review/analysis effort has been contracted by EPA to scientists (who do not work for EPA or industry) with extensive experience and expertise in the area of photochemical pollution occurrence and control. The first part of the overall effort, performed by the EPA Project Officer and reported in a scientific journal (1), was an explanatory analysis of the problem and definition of key issues, as viewed within the research component of EPA. The reports of the contractor expert/reviewer groups offering either resolutions of those issues or recommendations for additional research needed to achieve such resolutions are presented in the volumes composing this series.

This report presents the reviews/analyses prepared by the contractor experts on the issue of oxidant/ozone measurement. In the interest of completeness the report will include also an introductory discussion of the issue, taken from Part I. The reviews/analyses prepared by the contractor experts follow, along with the expert's comments on each other's reports.

THE ISSUE OF OXIDANT/OZONE MEASUREMENT

Basil Dimitriades and A. Paul Altshuller

Recent studies have resulted in some disconcerting evidence regarding the performances of the various oxidant/ozone measurement methods in existence (2-5). All potassium iodide (KI) procedures for either measuring ambient oxidant/ozone or for calibrating oxidant/ozone measurement methods were found to disagree with each other; the disagreement varied in degree depending on study or analyst. There was also disagreement between certain KI procedures and the more ozone-specific chemiluminescence and ultraviolet (UV) photometry methods. It is generally agreed that part of the disagreement is caused by the usual precision and accuracy errors associated with the various procedural steps and part with the difference in response specificity among the various methods. Thus, all KI methods show response to ozone (O_3) as well as to all vapors capable of oxidizing iodide ions or reducing iodine. Since these vapors and O_3 do not all cause equivalent responses, it follows that the KI measurement reflects not only the concentration but also the compositon — to the extent that such composition varies — of the responding vapor mixture. Further, the expected differences in response specificity are larger between the KI methods and the chemiluminescence and UV methods.

In the face of these differences in precision, accuracy, and response specificity among the various oxidant/ozone measurement methods, the obvious question relevant to this analysis is whether these imperfections in the analytical method invalidate any component of the oxidant control strategy. To explore this question, the functional relationship between the analytical method for oxidant/ozone and the oxidant control strategy, first, needs to be clarified.

Of the various components of the current oxidant control strategy the

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only one linked to the analytical method for oxidant/ozone is that related to the calculation of emission control requirements. Such calculation requires that the following three entities be defined:

- present air quality (PAQ), i.e., second highest 1-hour oxidant/ ozone in the reference year,
- desired air quality (DAQ), i.e., the National Ambient Air Quality Standard (NAAQS) for oxidant/ozone (0.08 ppm O_3), and
- a quantitative relationship between air quality and emission rates.

Of these, PAQ and DAQ are obviously the entities specifically linked to the oxidant/ozone measurement method. The preceding question, therefore, is now reduced to whether the analytical method imperfections invalidate (a) the PAQ data, and (b) the NAAQS for oxidant/ozone. Each of these two cases is examined separately.

To explore the impact of the analytical method imperfections upon the PAQ data, it might be useful to break down the impact of such imperfections into two parts: the impact arising from the usual precision and accuracy errors of the methods, and the impact arising from the nonspecificity of response. The precision/accuracy errors vary depending on (a) the method (e.g, KI methods, chemiluminescence, or UV photometry) and (b) the entity to be measured. To explain the latter, the magnitude of the precision/accuracy error is greater when the entity to be measured (i.e., PAQ) is expressed in terms of a single datum (e.g., second highest value) out of a population of data, than when it is the population average. Note, however, that the criterion for selecting the "second highest concentration" or the "average concentration" (or any other concentration) as the entity to be measured, is not the magnitude of the analytical error; rather, it is the health effects of oxidant/ozone. EPA has interpreted the health effects evidence available to mean that oxidant-related air should be defined in terms of a "highest" or "second highest" rather than "average" oxidant/ozone concentrations. *Whether this interpretation of the health effects of oxidants/ozone is correct or not is outside the scope of this analysis.* Thus, in the light of this discussion, the first specific

question that needs to be answered is:

1. Do the precision/accuracy errors invalidate the Federal reference method for oxidant/ozone? If yes, what method should be chosen instead?

The impact upon PAQ data of errors related to the specificity of response is far more complex than that of the precision/accuracy errors. The main complication arises from the rational requirement that the method measure that or those chemical species that have been found to have adverse health effects. However, since an important part of the health effects evidence is of epidemiological nature, *those species could not have been specified unequivocally.* This problem was circumvented by devising and using the concept of "surrogate" species, that is, species believed to represent those with the adverse effects. EPA initially proposed to promulgate that "oxidants" as measured by a specified KI method be used as the surrogate species; in the final promulgation, "oxidants" as measured by a (more ozone-specific) chemiluminescence method was pronounced the surrogate species. Rationally, measurement of PAQ by the chemiluminescence method should give lower results than by any KI method. However, there have been reports to be contrary. In the light of this latter dispute, and of the fact that the intended use of all methods is to measure surrogate species, the relevant question that must be answered next is:

2. Do the response-specificity errors invalidate the Federal reference method for oxidant/ozone? If yes, what method should be chosen instead?

The preceding two paragraphs dealt with the impact of the analytical method imperfections upon the PAQ data. The remaining discussion will deal with the impact upon the NAAQS for oxidant/ozone. The first obvious and direct question to be asked here is:

3. Do the imperfections of the analytical methods for oxidant/ozone invalidate the air quality standard for oxidant/ozone?

Following is a proposed answer to this question, and the reviewer judgment called for is on the correctness or incorrectness of this proposed answer.

The answer to this question, to a large degree, depends on the evidence and reasoning underlying the development of the air quality standard for oxidant/ozone. The underlying evidence is known to consist of associations between adverse effects and concentrations of "oxidants" measured by a variety of analytical methods. It should be noted that a major part of this associative evidence is not of a cause-effect nature. This means that the oxidant species responsible for the adverse effects could not have been unequivocally specified, which in turn means that the air quality standard did not have to be defined in terms of one or more specified oxidant species. Thus, the standard could be defined in terms of surrogate species, that is, in terms of a "response" given by any "oxidant" measurement method. In conclusion then, the validity of the qualitative definition of the NAAQS for oxidant/ozone should not be questioned.

The quantitative part of the (air quality) standard (i.e., the "0.08 ppm") can only be a result of analysis and interpretation of the health evidence available. Apparently the judgments made by the EPA experts with respect to the severity of the health effects and to the safety margin required were such that they justified use of the *0.08-ppm limit as measured by a specified analytical method (Federal Reference Method)*. These judgments may or may not be sound. However, this clearly pertains to another issue, namely the issue of health justification of the NAAQS-oxidant/ozone, and not to the issue of oxidant/ozone measurement. In conclusion, again, the imperfections of the analytical methods do not invalidate the 0.08-ppm of the oxidant/ozone standard, or, to put it differently, *cannot have a much different impact on the validity of a higher or lower standard*.

REVIEW AND ANALYSIS

James N. Pitts, Jr.

The following remarks deal specifically with questions raised on the issue of oxidant/ozone measurement in "Part I: Definition of Key Issues" taken from "An Analysis of the Evidence/Viewpoints Presented at the International Conference on Oxidant Problems."

As requested, these comments focus entirely on problems raised by the differences in precision, accuracy, and response specificity among the various oxidant/ozone measurement methods, and address "the obvious question relevant to this analysis is whether these imperfections in analytical method invalidate any component of the oxidant control strategy." The statements are the views of this reviewer and do not reflect the view of the Statewide Air Pollution Research Center (SAPRC) or agencies sponsoring its research.

Before specifically dealing with questions of measurement, it should be pointed out that establishment of air quality criteria for photochemical oxidant and reevaluation of the present air quality standard (AQS) involve questions not only about the precision and accuracy of the monitoring techniques for oxidant/ozone but also about the errors involved in measuring health effects. That is, when discussing the AQS it must be kept in mind that dose-response functions will contain errors not only in the "dose" but also in the determination of the human response to the pollutant. Clearly the errors in the latter may far exceed the errors involved in analytical measurements of the dose.

Let us now turn to the first question raised in this section of the issue paper:

1. "Do the precision/accuracy errors invalidate the Federal reference method for oxidant/ozone? If yes, what method should be chosen instead?"

Based on the weight of available evidence from a variety of sources, not only those presented at the International Conference on Photochemical Oxidant Pollution, but also on a series of studies conducted in other laboratories, it is this reviewer's opinion that the answer to this question is a *qualified* Yes.

In light of the intensive efforts directed to this question over the last several years by a variety of investigators, and because the results have been well reported, it seems unnecessary to go into detail here to justify this position. Indeed, a relevant discussion of the problem was given by Mr. Roger Strelow, Assistant Administrator for Air and Waste Management of the EPA, in his memo of December 18, 1975, to EPA Regional Administrators entitled "Errors in Ozone/Oxidant Monitoring System." This letter well summarizes the problem and seems definitive up to that time.

In terms of calibration of ozone monitoring apparatus, I would recommend either the UV method or gas phase titration. These techniques seem in excellent agreement, not only with each other but also with calibrations performed using infrared spectroscopy.

In terms of ambient air monitoring both the ultraviolet (UV) and chemiluminescent techniques seem acceptable, although somewhat expensive. There are, however, several relevant points made in the "Definition of Key Issues" on the use of such specific techniques, which are worth keeping in mind when answering this question. Thus both the UV and chemiluminescent instruments measure ozone specifically and do not measure ozone plus the "surrogate species" associated with it in "photochemical oxidant." The latter, i.e., "oxidant," may (or may not) produce health effects significantly greater than just O_3 in air. This point will be raised in more detail in the answer to the second question.

A second problem involves the rather high costs and complexity of UV and chemiluminescent instrumentation relative to typical potassium iodide (KI) analyzers. However, such considerations as to cost and complexity are beyond the scope of this discussion.

Finally, one must be concerned not just with the accuracy and precision of the calibration of various types of instruments but also with the overall accuracy and precision of analysis (either of specific ozone or of total oxidant) when the instrument is operating *in the field under ambient conditions* and is subject to all the "environmental" stresses present during actual air monitoring operations. This fact was well pointed out in Mr. Strelow's memo when he stated:

> Recently, the National Bureau of Standards (NBS) and EPA conducted a joint collaborative test designed to study the overall performance of typical ozone/oxidant monitoring systems in actual field use. These tests were conducted using an ozone generator designed by NBS capable of producing ozone at various concentrations. Field operators experienced in the use of the FRM for ozone were randomly selected to participate in the experiment. Ten generators were checked by the NBS laboratory, and the generated ozone concentrations were assayed by the NBKI procedure and verified by use of a gas-phase titration (GPT) procedure, another scientifically acceptable way to measure ozone. These generators were then shipped to ten different locations with instructions for the operators to prepare their monitoring instruments as they normally would, and then to measure the output from the ozone generator. Upon completion of the testing, the ten generators were returned to NBS where confirmation was made that generator performance had not varied during shipment to and from the field.
>
> The surprising results from the joint collaborative study revealed that the monitoring system as a whole, (NBKI calibration procedure, chemiluminescence monitor, and operator performance) consistently have a significant negative bias (i.e., indicated an ozone concentration less than the NBS determined output of the generator). Also there were wide variations between the performance of the systems from the different field locations, with an average percentage difference between the observed generator output and the NBS determined output ranging between 16 and 30 percent over the range of concentrations investigated. Thus while the NBKI calibration method has been shown to have a positive bias under ideal conditions, the collaborative study indicates that the collective performance of the NBKI procedure, the chemiluminescent monitor, and the average field operator results in a significant and variable negative bias in the monitoring data. Unfortunately this study did not address errors in the individual components of the overall system.

Tests similar to those cited by Mr. Strelow should also be carried out in the field with analytical systems employing UV monitors, as pointed out above. Of course, this may already have been done, and if so it will be interesting to see the results.

It is perhaps worth reemphasizing that wet KI monitors actually measure photochemical oxidant; they are not specific for ozone. Thus approximately 15% of the nitrogen dioxide (NO_2) and of the peroxyacetyl nitrate (PAN) present in photochemical smog will be read as oxidant. Conversely, any sulfur dioxide (SO_2) in the air will *lower* the total oxidant readings, and with 100% efficiency.

In this regard the statement in Part I, "rationally, measurement of PAQ by the chemiluminescent method should give lower results than by any KI method," is not strictly correct. For example, if a significant amount of SO_2 is present along with ozone in ambient air, and only small amounts of NO_2 are present the chemiluminescent instrument would, in fact, read *higher* than the KI instrument. It is my understanding that this situation does in fact occur in certain areas. Also, I understand that for certain KI instruments "scrubbers" are provided to remove the SO_2.

While on the subject, it seems to this reviewer that oxidant measurements in the archival data banks throughout the country should be corrected for positive interference if NO_2 is present (ambient concentrations of PAN are generally low enough relative to ozone that the correction for PAN is minor) and for negative interference if significant levels of SO_2 coexist with the O_3. Also, old data should be carefully screened to see if the appropriate correction from phenolphthalein to KI has been made.

Despite certain problems with the KI method, it seems important for at least two reasons to retain a wet KI oxidant monitoring instrument along with specific instruments for O_3, NO_2, and SO_2 (as well as others) in air monitoring stations throughout the U.S. and, and indeed, the world. Thus, millions of data have been accumulated over the last two decades of measurements of oxidant ambient air quality. It would be a shame not to continue using the relatively

inexpensive KI technique as a "backup" and so that one can directly correlate (admittedly with appropriate corrections) current and future ambient air data for oxidant/ozone with those obtained, for example, in the 1960s.

A second, and related, point is that despite problems with accuracy and precision the wet KI method does give some indication of the concentration not only of ozone but also of associated surrogate species that may have health effects. This point has been raised earlier.

Thirdly, it is my understanding that most, if not all, of the data that were used to generate the dose-response functions, upon which health effects of photochemical oxidant were based (i.e., in the Air Quality Criteria Document) and upon which the present air quality standard is based, were carried out using a wet method for total oxidant. Therefore, if the response portion of dose-response functions is based upon data for humans in which, for example, a KI method was used to determine the exposure of a person to oxidant, then the *dose* portion of that curve should be conducted either with the same type of instrumentation or at least instrumentation that can be reliably related to that used in the response portion (of course, with appropriate correction factors).

Questions of the latter type obviously involve the analytical techniques by which the effects of oxidant on humans were elucidated by medical researchers in the past. As stated earlier, this reviewer is not competent to judge the validity of such health effects studies. However, he urgently recommends that a panel of medical experts, including several chemists familiar with the analytical techniques used for oxidant measurements some years ago when these health effects studies were carried out, be assembled to examine this entire question very critically, before a decision is made on the validity of the present AQS for oxidant.

For example, in the Air Quality Criteria Document for Photochemical Oxidant, apparently the Pasadena asthmatic studies were discussed on the assumption that the oxidant levels were measured by the phenolphthalein method. Therefore, apparently these levels were divided by two to convert

them to equivalent potassium iodide values. It is my understanding from Professor Edgar Stephens of SAPRC that, "It has since been established that the original study was *not* done against phenolophthalein but against KI (L.A. style) so this division by two was improper."

This referee is not qualified to comment on this particular issue but Professor Stephens is, and he raises a very interesting point. Indeed, it is precisely this kind of analysis of "historical" analytical and medical data by a combined panel of experts, as suggested earlier, that is much needed.

2. "Do the response-specificity errors invalidate the Federal Reference Method for oxidant/ozone? If yes, what method should be chosen instead?"

This reviewer is not sure of the intent or thrust of this question. As suggested in the earlier discussion, if one measures photochemical oxidant in ambient air with instruments specific for ozone but conducts health effects studies in which total oxidant is measured, then the answer to Question 2 is Yes. That is, humans may react in one way to the surrogate mixture defined as "photochemical oxidant" and quite differently to exposures to simulated atmospheres containing only ozone. Thus, if health effects studies are to be based on exposures of humans to ozone alone, then the KI Federal reference method that measures oxidant may be invalid in this context. In short, the analytical monitoring techniques used to determine human exposure to ozone or oxidant in the laboratory must be entirely consistent with analytical monitoring techniques used to determine human exposure to ozone or oxidant in real ambient air.

3. "Do the imperfections of the analytical methods for oxidant/ozone invalidate the air quality standard for oxidant/ozone?"

As we have seen, the answer to Question 3 can be Yes or No, depending on the situation. The answer is No if *self-consistent* measures for determining the levels of exposures of humans to ozone *or* oxidant in both the laboratory and in ambient air are employed by local, state, and federal agencies and by

researchers in other organizations (including industry and universities) who are involved with establishing dose-response effects. If there has not been internal consistency between all investigators involved in establishing dose-response functions and in interpreting previously established functions of this type, then the answer is clearly Yes; the air quality standard for oxidant/ozone will be invalid.

Finally, let us examine the concluding statement on the issue of oxidant/ozone measurement:

> In conclusion, again, the imperfections of the analytical methods do not invalidate the 0.08-ppm part of the oxidant/ozone standard, or, to put it differently, *cannot have a much different impact on the validity of a higher or lower standard*.

This statement may or may not be correct. If, for example, the corrections made to convert ozone levels measured years ago by the phenolphthalein technique to the potassium iodide method were incorrect, this could have an impact on the validity of a higher or lower AQS for oxidant/ozone. Therefore, such a statement has to be examined very carefully.

Actually, it is this researcher's impression, strictly as a non-expert in the health effects area, that the major question dealing with the accuracy of the present air quality standard for oxidant lies in assessing the magnitude of the errors associated with the determination of human response to oxidant/ozone rather than with the analytical method used for establishing ozone or photochemical oxidant concentrations. That is, assuming that in the Federal reference method there may be errors in accuracy and precision up to perhaps 30% (and this is just an assumption, not necessarily a fact), it is this reviewer's feeling that such an error may be relatively small compared to errors associated with the establishment of the health impact of photochemical oxidant *or* ozone on man. Of course, this is the point made initially in this critique. It should be stressed, however, that even if this is true it should not be used as an excuse to tolerate inaccurate or imprecise techniques for measuring levels of oxidant/ozone in simulated or real atmospheres.

REVIEW AND ANALYSIS

George Su

I have reviewed the papers by Paur, Stevens, and Flamm (2); Hodgeson, Hughes, Schmidt, and Bass (3); Paur et al. (4); DeMore et al. (5); and Neal et al. (6). Data from all but the last paper presented convincing evidence that the neutral buffered KI method as it is used now is inaccurate and gives values generally high by as much as 30%. Furthermore, they showed that the long path UV photometric and gas phase titration calibration methods are in good agreement with each other, and are good, valid methods for calibration and should not have problems with reproducibility. However, DeMore et al. suggested that the UV photometric method (published in ASTM) should be the "preferred primary standard" because the gas phase titration method at the time was considered to be "less well established." Both methods are specific for ozone. I have but one minor reservation regarding these papers — the concentrations studied are mostly above the 0.1 ppm level. I would have preferred to see a few more concentrations below 0.1 ppm, which is where most oxidant concentrations are observed.

I am convinced that the neutral buffered KI method is not acceptable because it gives irreproducible results as well as excessively high levels. Our own laboratory indicates that this method varies as much as 10 to 30%; and apparently it was recognized by Boyd et al. (Analytical Chemistry) as far back as 1970 that the neutral buffered system tends to release excessive amounts of iodine, thereby causing the high readings. Hodgeson et al. also reported a time-dependence factor over a 30-minute period for color development for the neutral buffered KI method. In our own laboratory, we see no time dependence within a 30-minute period. Again, discrepancies of this type between laboratories underscored the difficulties with the neutral buffered KI method.

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The boric acid KI method appears extremely promising and would not require highly sophisticated and expensive instrumentation as in the case of UV photometry and gas phase titration. Obviously, this method deserves more intensive studies and experimentation and, if proven to be as accurate and reproducible as it apparently is in these studies, then it, along with the UV photometry and gas phase titration, should be promulgated as reference methods.

Personally, I am in favor of gas phase titration as a calibration method for our own laboratory for several reasons:

- It can also be used, with minor changes, to calibrate NO_x analyzers (already promulgated).
- The NO_x analyzer and the ozone meter required in this calibration system can also be used for monitoring when not being used as a primary calibration unit.
- The long path UV photometry requires considerable lab space and may be more difficult to operate in our laboratory.

We have already requisitioned a gas phase titration system for calibration of our ozone meters, in spite of the fact that this method has not been officially promulgated, because we are convinced of the validity of this method and that, even if it were not promulgated as a reference or equivalent method, this calibration system can still be used to calibrate our NO_x analyers.

The paper comparing chemiluminescent and KI methods seems to me to be of little value. The authors observed higher ozone than total oxidant, which by definition should be impossible because ozone is only part of the total oxidant. The KI method is well documented to almost always read higher than the chemiluminescence method.

I suspect that the reason for the lower total oxidant reading is the chromium trioxide scrubber that is used with the Beckman Acralyzer using the neutral buffered KI method. The only merit I see in this paper is that it points out once again the difficulties involved in using the neutral buffered KI method.

In summary, based on the data presented in these papers, I am satisfied that both the UV photometry and the gas phase titration methods are valid and should be accepted by EPA as reference calibration methods. The neutral buffered KI method should be withdrawn as a reference method.

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